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High-quality Ge films on Si substrates using Sb surfactant-mediated graded SiGe buffers

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High-quality Ge films were grown on Si substrates by solid-source molecular beam epitaxy using SiGe graded layer and Sb surfactant-mediation technique. Transmission electron microscopy measurements show that samples grown using this method have a lower threading dislocation density than those grown by other typical methods, such as grading at high temperature (700 °C) only, grading at intermediate temperature (510 °C) only, and the use of low temperature Si buffer. A relaxed Ge film on a 4-μm-thick graded buffer was grown and shown to have a threading dislocation density of $5.4\times10^5\ \mathrm{cm}^{-2}$ and surface roughness of 35 Å. Ge $p-i-n$ diodes were fabricated and tested. Under a reverse bias of 1 V, the $p-i-n$ Ge mesa photodiodes exhibit a very low dark current density of 0.15 mA/cm^2. © *2001 American Institute of Physics.*
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The rapid development of optical communications demands low cost optical components that operate in the near infrared windows of fiberoptic transmission (1.3 and 1.55 μm). Pure Ge photodetector integrated on Si is one of the promising candidates for this purpose, owing to its band gap of 0.67 eV and full compatibility with modern Si technology. Nevertheless, the large-scale practical application of this kind of device is not yet realized due to the difficulty in the growth of high quality of pure Ge films on Si with a low threading dislocation density and smooth surface. One earlier attempt was done by Luryi, Katalsky, and Bean[1] in the early 1980s where only an 1800-Å-thick step-graded SiGe buffer layer was employed between the top $p-i-n$ Ge film and the underlying Si substrate. The leakage current of the diodes was very high ($\approx$200 mA/cm^2 at -1 V) due to the high density of dislocations. Samavedam *et al.*[2] fabricated improved Ge photodiodes using a thick graded SiGe buffer ($\geqslant$10 μm) with an intermediate chemical mechanical polishing step. The leakage current was reduced to 0.2 mA/cm^2 under a reverse bias of 1 V. Another interesting approach was made by Sutter, Kafader, and Von Kanel[3] and Colace *et al.*,[4,5] in which a pure Ge film was directly grown on Si by using a hydrogen-surfactant mediation step followed by a post-growth cyclic thermal annealing treatment. Recently, we have also shown high-quality relaxed SiGe buffers with a very low threading dislocation density and smooth surface by combining the use of a graded buffer and an Sb surfactant mediation technique.[6] The high quality arises from the optimized relaxation of the structure, where not only threading dislocations but also Sb are used to relieve stress caused by the 4% mismatch between Si and Ge.

In this letter, we study systematically the Sb surfactant-mediated graded buffer layer growth technique, which leads eventually to the growth of high-quality Ge films on Si using SiGe buffers with steep grading rates. $P-i-n$ Ge diodes were fabricated on a 4 μm SiGe buffer and these diodes exhibited very low leakage current and a high external quantum efficiency.

A solid-source molecular beam epitaxy was used for sample growth. In order to show the effect of Sb surfactant mediation on the quality of the buffer, we compared with four samples having different growth conditions. All samples have the same top-layer Ge molar fraction of 0.5. Samples A, B, and C consist of a 2 μm graded SiGe with a grading rate of 25% Ge per 1 μm, followed by a 0.3 μm $\mathrm{Si_{0.5}Ge_{0.5}}$ buffer. Sample A was grown at 510 °C. One ML Sb was also deposited and no Sb pre-deposition was used for samples B, C, and D. Samples B and C were grown at 700 and 510 °C, respectively. Sample D was simply a low-temperature SiGe assisted 200-nm-thick $\mathrm{Si_{0.5}Ge_{0.5}}$ film. The growth temperature cycle used was the same as that in the literature.[7] Figure 1 shows weak beam dark field transmission electron microscopy (TEM) images of the samples. For sample A, the dislocations occur near the bottom of the buffer and the top $\mathrm{Si_{0.5}Ge_{0.5}}$ layer is dislocation free. For samples B, C, and D, however, there are high densities of threading dislocations penetrating to the top $\mathrm{Si_{0.5}Ge_{0.5}}$ layer. A quantitative study of threading dislocations by the Schimmel etch pit method[8] shows that the threading dislocation density of $1.5\times10^4\ \mathrm{cm}^{-2}$ is obtained for sample A, while samples B, C, and D have threading dislocation densities as high as $10^9\ \mathrm{cm}^{-2}$. Surface roughness measurements on as-grown samples by AFM show that the root mean square (rms) roughness of 20, 161, 38, and 27 Å is obtained for samples A, B, C, and D, respectively.

In order to gain further insight into Sb mediation, we have investigated the grading rate dependence on the resulting threading dislocation density and surface roughness. A series of samples were grown at 510 °C by grading Ge from 0% to 50% Ge with a 0.2-μm-thick $\mathrm{Si_{0.5}Ge_{0.5}}$ layer on top. An Sb layer 1 ML thick was predeposited. Figure 2(a) shows the threading dislocation density as a function of grading rate. The threading dislocation density decreases with the decrease of grading rate. For comparison, the threading dis-

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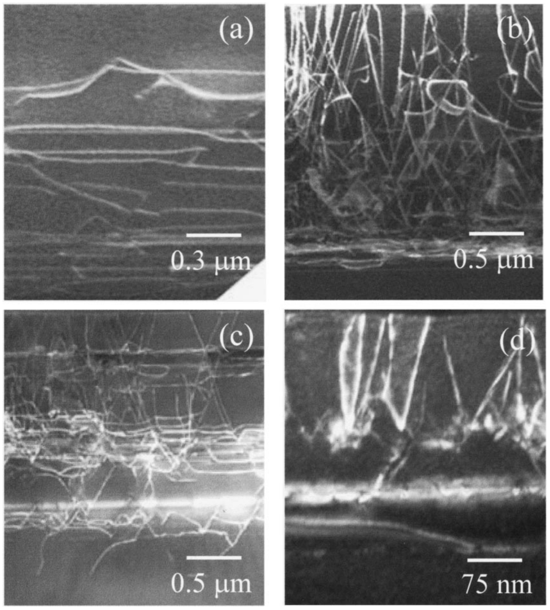

FIG. 1. Weak beam dark field cross-sectional TEM images of (a) sample A: Sb-mediated graded $Si_{0.5}Ge_{0.5}$ film at 510 °C, (b) sample B: Graded $Si_{0.5}Ge_{0.5}$ film at 700 °C, (c) sample C: Graded $Si_{0.5}Ge_{0.5}$ film at 510 °C, and (d) sample D: Low-temperature SiGe assisted $Si_{0.5}Ge_{0.5}$ film. Samples A, B, and C have the same buffer layer grading rate of 25% Ge per 1 μm and a 0.3 μm $Si_{0.5}Ge_{0.5}$ cap layer. The thickness of $Si_{0.5}Ge_{0.5}$ film of sample D is 200 nm.

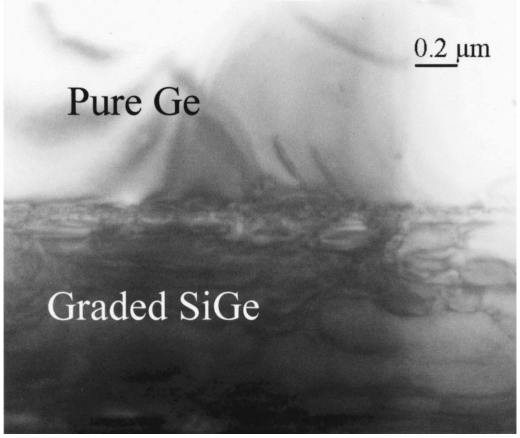

FIG. 3. Bright-field cross-sectional TEM image of the $p-i-n$ Ge film with a 4 μm Sb-mediated graded SiGe buffer. From the TEM point of view, the pure Ge layer is free of dislocations.

location densities of samples B and C are shown as well. Figure 2(b) shows the rms roughness as a function of grading rate. The surface becomes one order of magnitude smoother compared with those samples grown at higher temperatures. In addition, the lower grading rate is used, the smoother surface it becomes.

It is interesting to discuss why Sb surfactant improves the film quality markedly. For graded SiGe films grown at high temperature ($\geqslant$700 °C), there are at least certain amounts of threading dislocations (10^6 cm^{-2} dislocation density for a graded layer with 10% Ge per 1 μm grading rate) to compensate misfit strain and relax the film.[9] For relaxed SiGe films grown on low-temperature Si, the film relaxation relies on the termination of threading dislocations by point defects produced in the low temperature Si layer.[7,10] Thus to obtain low-dislocation-density film, a certain amount of point defects is needed in the low-temperature Si layer by optimizing the Si layer thickness and its growth temperature or by using other methods. For graded SiGe films grown only at intermediate temperature ($\sim$500 °C), misfit dislocations cannot move effectively during film growth and once the film builds enough strain energy, it cracks abruptly by generating large amounts of threading dislocations. As the film continues to grow, thickness and Ge molar fraction increases and the strain builds up again. The relief of strain will take place by generating threading dislocations again at the upper layer. Graded SiGe films grown using Sb surfactant mediation at intermediate temperature ($\sim$500 °C) are of high quality because Sb helps the motion of misfit dislocations during growth, eventually decreasing the threading dislocation density in the film.

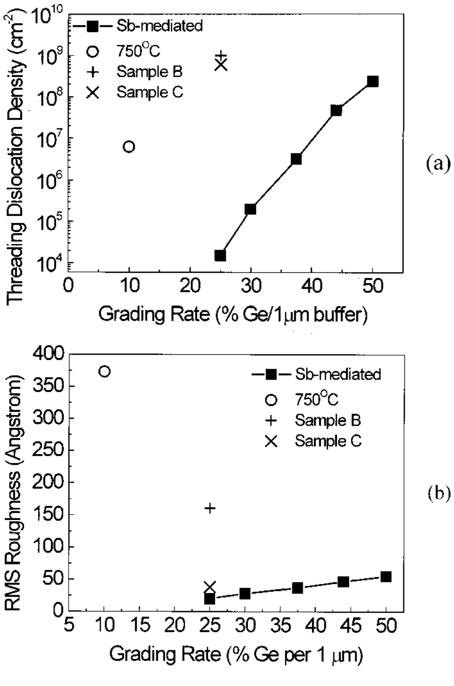

FIG. 2. (a) Threading dislocation density, and (b) rms surface roughness as a function of grading rate of Sb-mediated graded SiGe film. The data of 750 °C are from Ref. 13, indicating that a threading dislocation density of 6.3×10^6 cm^{-2} is obtained for graded buffers at 750 °C.

Using the abovementioned method, two pure Ge samples were then grown on Sb-mediated graded SiGe buffers. The structures consist of the following layers: 100-nm-thick Si buffer, linearly graded $Si_{1-x}Ge_x$ with x from 0 to 1 (the top 0.6-μm-thick buffer was doped with Sb of 0.7–1 $\times10^{17}$ cm^{-3} to form n layer), 0.8-μm-thick undoped Ge and 0.1-μm-thick B-doped p^+ Ge with a doping density of 5×10^{18} cm^{-3}. The only difference between the two samples is the thickness of the linearly graded $Si_{1-x}Ge_x$ buffer, which is 1 and 4 μm, respectively. Figure 3 shows the bright-field cross-sectional TEM image of the sample with the 4-μm-thick buffer. A large density of threading dislocations is clearly seen in the graded buffer region only. In other words, the top 0.9 μm pure Ge film is of high quality with a very low threading dislocation density, beyond the ability of the TEM method.

In order to characterize the low dislocation density, Nomarski microscopy was used to observe a defect selectively etched pure Ge sample with the 4 μm graded buffer.

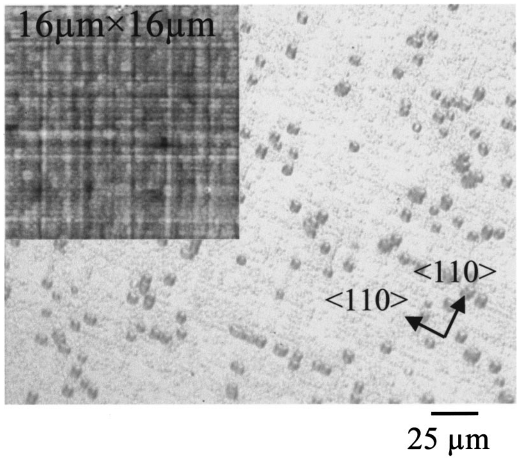

FIG. 4. Nomarski image of the etched Ge film with a 4 μm buffer indicating I-coated pits arising from threading dislocations. The threading dislocation density is estimated to be 5.4×10^5 cm^{-2}. The inset shows the as-grown sample surface. The surface roughness is determined to be 35 Å.

Figure 4 shows a typical result. The selective etchant used was a mixture of CH_3COOH, HNO_3, HF, and I_2.[11] The threading dislocation density was obtained by counting the I-decorated pits on the surface which were determined to be 5.4×10^5 cm^{-2}. This number is about one order of magnitude larger than that from the previous results of the buffer layers graded to 50% Ge with the same grading rate (sample A), and may be due to the formation of rougher surface and more dislocation pile-ups in the thicker layers.[12] The inset of Fig. 4 shows an atomic force microscopy image of an as-grown sample surface with the 4 μm graded buffer. Long and straight misfit dislocation lines are evident. The rms surface roughness was measured to be 35 Å.

These two samples were fabricated into Ge $p-i-n$ mesa diodes 100 μm×200 μm in size. Plasma enhanced chemical vapor deposition SiO_2 was used for passivation. Figure 5 shows $I-V$ measurement results. The dark current density at a reverse bias of 1 V was determined to be 0.15 and 3.44 mA/cm^2 for the Sb-mediated samples with the 4 and 1 μm buffer, respectively. It is encouraging to note that the dark current density from the sample with a 100% Ge per 1 μm steep grading rate was several times lower than the previously reported values of 200 mA/cm^2[1] and 50 mA/cm^2.[3] The sample with a 25% Ge per 1 μm grading rate exhibits a very low dark current density, close to the ideal dark diffusion current density of 0.03 mA/cm^2 based on our doping profile. Minority carrier lifetime τ_p of 10^{-7} s was used in our calculation. The internal quantum efficiency was measured to be as high as 70% at 1.55 μm for the diodes with the 4 μm SiGe buffer. The detector response as determined by the RC constant was about 2.3 GHz. Detailed spectral photoresponse and frequency performance will be reported elsewhere.

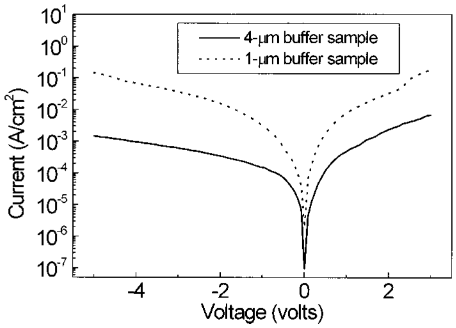

FIG. 5. Current–voltage characteristics of $p-i-n$ Ge diodes fabricated on two Sb-mediated samples with 4 and 1 μm buffer, respectively. The dark current density is determined to be 0.15 and 3.44 mA/cm^2 at the reverse bias of 1 V, respectively.

In summary, we have demonstrated the growth of high-quality steep graded SiGe layers and the fabrication of Ge $p-i-n$ photodiodes by using both Sb surfactant mediation and graded buffer technique. By comparing with those samples using other methods, the Sb-mediated samples exhibit a lower threading dislocation density and smoother surface. Ge $p-i-n$ diodes fabricated by this method show very low dark current density of 0.15 mA/cm^2 at a reverse bias of 1 V. These results suggest the potential applications of integrated 1.55 μm Ge detectors on Si substrates.

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[1] S. Luryi, A. Katalsky, and J. C. Bean, IEEE Trans. Electron Devices **ED-31**, 1135 (1984).
[2] S. B. Samavedam, M. T. Currie, T. A. Langdo, and E. A. Fitzgerald, Appl. Phys. Lett. **73**, 2125 (1998).
[3] P. Sutter, U. Kafader, and H. Von Kanel, Sol. Energy Mater. Sol. Cells **31**, 541 (1994).
[4] L. Colace, G. Masini, F. Galluzzi, G. Assanto, G. Capellini, L Di Gaspare, E. Palange, and F. Evangelisti, Appl. Phys. Lett. **72**, 3175 (1998).
[5] L. Colace, G. Masini, G. Assanto, H.-C. Luan, K. Wada, and L. C. Kirmerling, Appl. Phys. Lett. **76**, 1231 (2001).
[6] J. L. Liu, C. D. Moore, G. D. U'ren, Y. H. Luo, Y. Lu, G. Jin, S. G. Thomas, M. S. Goorsky, and K. L. Wang, Appl. Phys. Lett. **75**, 1586 (1999).
[7] M. Bauer, K. Lyutovich, M. Oehme, E. Kasper, H.-J. Herzog, and F. Ernst, Thin Solid Films **369**, 152 (2000).
[8] D. Schimmel, J. Electrochem. Soc. **126**, 479 (1979).
[9] E. A. Fitzgerald, Y.-H. Xie, D. Monroe, P. J. Silverman, J. M. Kuo, A. R. Kortan, F. A. Thiel, and B. E. Weir, J. Vac. Sci. Technol. B **10**, 1807 (1992).
[10] Y. H. Luo, J. Wan, R. L. Forrest, J. L. Liu, G. Jin, M. S. Goorsky, and K. L. Wang, Appl. Phys. Lett. **78**, 454 (2001).
[11] H.-C. Luan, D. R. Lim, K. K. Lee, K. M. Chen, J. G. Sandland, K. Wada, and L. C. Kirmerling, Appl. Phys. Lett. **75**, 2909 (1999).
[12] S. B. Samavedam and E. A. Fitzgerald, J. Appl. Phys. **81**, 3108 (1997).
[13] M. T. Currie, S. B. Samavedam, T. A. Langdo, C. W. Leitz, and E. A. Fitzgerald, Appl. Phys. Lett. **72**, 1718 (1998).